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Volumetric Properties of Alkali Metal p-Toluenesulphonates in Water as a Function of Temperature

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Abstract

Density data are presented for alkaline salts of p-toluenesulphonic acid at temperatures from 5 to 40 ^{O}C up to concentrations of ~2 mol/kg. The apparent molar volumes, $V_{2\Phi}$, were calculated for these solutions from the density measurements. The apparent molar volumes were fitted to the equation of Redlich and Meyer to determine two important parameters: i) the apparent molar volume at infinite dilution, $V_{2\Phi}^{o}$, and ii) the deviation constant b_V. At 25 ^{O}C the additivity rule of the individual ionic contributions was confirmed. Further, $V_{2\Phi}^{o}$ increases with increasing temperature for all the salts, while the parameters b_V monotonically decrease from positive to negative values (in the order Li<Na<K<Rb<Cs) as the temperature is increased. The effect of temperature on the apparent molar volumes of the p-toluenesulphonates in water at infinite dilution is similar to that of other simple electrolytes.

Key words: Alkaline p-Toluenesulphonates; Apparent Molar Volume; Density; Apparent Molar Expansibility.

Dedicated to the memory of Prof. Savo Lapanje

Introduction

Thermodynamic properties of electrolyte solutions expressed as apparent or partial molar quantities are useful in characterizing solute-solvent and solute-solute interactions. One approach toward a deeper understanding of interactions in polyelectrolyte solutions is to study the monomer system. It is reasonable to expect the electrochemical properties of the sulphonic group in polystyrenesulfonate solutions to be similar to those in low molecular analogues, i.e. various substituted benzenesulphonic acids and their salts [1]. Study of the monomer system is, moreover, facilitated by the fact that accurate theories are available for the analysis of experimental data on solutions of simple electrolyte.

The excess thermodynamic properties of electrolyte solutions, i.e. osmotic coefficients, heats of dilution, or volume changes on dilution, are determined by the ion-ion and ion-solvent interactions. Additional information about interactions in solution may be obtained by studying the system at various temperatures since different interaction potentials have different temperature dependencies [2]. Recently, the heats of dilution (ΔH_D, $c \rightarrow 0.002$ mole-dm^{-3}) at various temperatures have been measured [3] for aqueous solutions of the alkaline salts of p-toluenesulphonic acid. In the another publication [4], a preliminary theoretical analysis of the osmotic coefficients, heats of dilution and volume changes on dilution based on Friedman's theory [5] was presented. Unfortunately, except for the osmotic coefficients and heats of dilution, a complete investigation of the concentration dependence of other properties of the alkali p-toluenesulphonates is lacking. In the literature we found the partial molar volume data of p-toluenesulphonic acid and its sodium salt for the temperature of 25 ^{O}C [6], but no measurements for other temperatures were presented so far. Since the concentration dependence of the apparent or partial molar volume over a sufficiently wide range of temperature is needed to verify the theoretical models of electrolyte solution, we measured the densities of Li, Na, K, Rb and Cs salts of p-toluenesulphonic acid in water at 5, 15, 25, and 40 ^{O}C. From the concentration dependence of the apparent molal volumes and with the use of the Redlich-Meyer equation [7], the apparent molal volumes at infinite dilution and the parameter b_V were determined. The differences in values of these quantities between various salts were interpreted with respect to

structural interactions[8-10]. Note that extensive reviews of the volumetric properties of electrolyte solutions have been published by Millero [11,12].

Experimental

Toluene-4-sulphonic acid monohydrate (or p-toluenesulphonic acid monohydrate, abbreviated to HTS.H_2O, Merck 99%) was used as a starting material for preparation of alkaline (Li, Na, K, Rb, Cs) p-toluenesulphonates (TS). All salts were prepared by neutralization of an acid solution by the corresponding metal hydroxide or carbonate until a pH of about 5 was obtained. The concentration of the acid stock solution was determined by potentiometric titration, while the concentrations of stock salt solutions were measured spectrophotometrically. In all the experiments water doubly distilled in quartz was used.

The densities of solution *d* were measured at a given temperature using a Paar digital precision density meter, Model DMA 620, with a reproducibility of 10^{-5} g-cm^{-3}. About 10 measurements at each concentration were carried out for each solution. Calibrations at each temperature were made with pure water [13], and with dry air at least twice a day. The temperature of the cell compartment was controlled to ±0.01 ^{O}C using a Heto circulating thermostat. The temperature was measured in a water bath with a platinum resistance thermometer (Degusa Pt1000) and a thermistor inserted into the cell of the density meter. The water bath and the density meter were located so that a stream of water at constant temperature travelled between them.

The apparent molar volumes $V_{2\Phi}$ were calculated from the densities *d* using [12]

$$V_{2\Phi} = \frac{M_2}{d} + \frac{1000\left(d^0 - d\right)}{mdd^0} \qquad (1)$$

where d^0 is the density of pure water, *m* the molality and *M* the molar mass of the solute.

The experimental error in $V_{2\Phi}$, which stems from uncertainties in the density measurements, exceeds that from the uncertainties in concentration. The error was

estimated to be < ± 1 cm^3-mol^{-1} at the lowest measured concentration and decreases with increasing concentration.

Results

Experimentally obtained densities are given in Table I for each of the salts and the acid, as a function of molality and temperature. Table I also lists the apparent molar volumes calculated by Equation (1).

TABLE I. Densities and Apparent Molar Volumes of Aqueous Alkaline p-Toluenesulphonate Solutions as a Function of Concentration at Various Temperatures.

HTS 5 ^{O}C

m [a]	d [b]	$V_{2\Phi}$ [c]
0.0104	1.00055	115.56
0.0505	1.00280	115.66
0.1053	1.00582	115.86
0.5559	1.02913	116.34
1.0573	1.05208	116.82
1.1815	1.05752	116.77
1.3301	1.06360	116.92
1.4162	1.06717	116.89
1.6218	1.07514	117.05

HTS 15 ^{O}C

m	d	$V_{2\Phi}$
0.0094	0.99961	118.42
0.0466	1.00159	118.61
0.0764	1.00316	118.64
0.2959	1.01434	118.96
0.6487	1.03109	119.14
0.8232	1.03892	119.15
1.0903	1.05034	119.16
1.4221	1.06360	119.22
1.8729	1.08042	119.16
2.1339	1.08952	119.13

[a] Units: mol-kg^{-1}
[b] g-cm^{-3}
[c] cm^3-mol^{-1}.

HTS 25 ^{O}C

m	d	$V_{2\Phi}$
0.0095	0.99754	120.69
0.0471	0.99946	120.90
0.0775	1.00099	121.07
0.2984	1.01177	121.28
0.6561	1.02801	121.47
0.8321	1.03548	121.56
1.1057	1.04664	121.55
1.4359	1.05937	121.46
1.9029	1.07577	121.50
2.1728	1.08473	121.44

HTS 40 ^{O}C

m	d	$V_{2\Phi}$
0.0479	0.99462	122.38
0.0776	0.99608	122.50
0.3024	1.00680	122.76
0.6540	1.02235	123.01
0.8312	1.02980	122.97
1.1198	1.04118	123.06
1.4590	1.05380	123.04
1.9248	1.06967	123.07
2.2040	1.07871	122.97

LiTS 5 ^{O}C

m	d	$V_{2\Phi}$
0.0109	1.00065	114.94
0.0505	1.00313	115.08
0.1021	1.00631	115.23
0.4326	1.02575	115.54
0.9349	1.05262	115.72
1.2196	1.06659	115.79
1.3115	1.07085	115.87
1.5196	1.08043	115.86
1.6724	1.08713	115.91
1.9019	1.09687	115.94

LiTS 15 ^{O}C

m	d	$V_{2\Phi}$
0.0105	0.99973	117.92
0.0515	1.00218	118.04
0.1069	1.00544	118.13
0.5756	1.03129	118.45
0.9694	1.05104	118.46
1.2667	1.06510	118.29
1.4204	1.07192	118.31
1.5718	1.07846	118.31
1.7285	1.08518	118.22
1.8988	1.09236	118.07

LiTS 25 ^{O}C

m	d	$V_{2\Phi}$
0.0105	0.99766	120.13
0.0520	1.00004	120.36
0.1067	1.00315	120.42
0.5777	1.02817	120.69
0.9725	1.04729	120.61
1.2742	1.06087	120.56
1.4570	1.06879	120.46
1.5987	1.07463	120.47
1.7865	1.08219	120.43
1.9264	1.08777	120.34

LiTS 40 ^{O}C

m	d	$V_{2\Phi}$
0.0106	0.99282	121.38
0.0517	0.99515	121.60
0.1073	0.99825	121.69
0.5774	1.02277	122.03
0.9804	1.04182	122.04
1.2777	1.05494	121.96
1.4318	1.06146	121.90
1.5950	1.06806	121.91
1.7701	1.07507	121.81
1.9185	1.08080	121.76

NaTS 5 ^{O}C

m	d	$V_{2\Phi}$
0.0107	1.00081	114.78
0.0509	1.00397	115.05
0.1004	1.00781	115.17
0.4287	1.03190	115.98
0.9321	1.06507	116.74
1.0858	1.07434	116.98
1.2408	1.08343	117.13
1.5461	1.10020	117.56
2.0830	1.12727	118.04

NaTS 15 ^{O}C

m	d	$V_{2\Phi}$
0.0186	1.00052	117.72
0.2563	1.01797	118.35
0.5133	1.03561	118.76
0.7930	1.05359	119.03
1.0755	1.07055	119.27
1.3229	1.08448	119.49
1.4769	1.09276	119.61
1.6947	1.10408	119.72
1.8991	1.11412	119.88
2.0779	1.12258	119.99

NaTS 25 ^{O}C

m	d	$V_{2\Phi}$
0.0186	0.99843	119.93
0.2559	1.01535	120.57
0.5114	1.03243	120.86
0.7846	1.04949	121.15
1.0731	1.06634	121.37
1.3143	1.07963	121.49
1.4768	1.08819	121.56
1.6828	1.09855	121.69
1.8873	1.10851	121.74
2.0727	1.11714	121.80

NaTS 40 ^{O}C

m	d	$V_{2\Phi}$
0.0184	0.99357	120.78
0.2519	1.01010	121.40
0.5025	1.02677	121.64
0.7816	1.04413	121.86
1.0474	1.05966	122.00
1.2918	1.07319	122.07
1.4386	1.08099	122.10
1.6535	1.09191	122.19
1.8519	1.10167	122.19
2.0246	1.10983	122.21

KTS 5 ^{O}C

m	d	$V_{2\Phi}$
0.0096	1.00080	123.81
0.0514	1.00436	124.10
0.1008	1.00854	124.18
0.4309	1.03479	125.13
0.8165	1.06248	125.85
0.9504	1.07153	125.98
1.0973	1.08107	126.15
1.2625	1.09121	126.48
1.4109	1.10022	126.55
1.5724	1.10956	126.71

KTS 15 ^{O}C

m	d	$V_{2\Phi}$
0.0133	1.00020	127.59
0.0639	1.00433	127.79
0.1337	1.00992	128.01
0.6580	1.04850	128.90
0.8195	1.05931	129.09
1.0002	1.07092	129.25
1.1277	1.07882	129.33
1.2541	1.08641	129.43
1.4055	1.09512	129.59
1.6109	1.10656	129.70

KTS 25 ^{O}C

m	d	$V_{2\Phi}$
0.0134	0.99811	130.57
0.0645	1.00214	130.83
0.1342	1.00752	131.00
0.6682	1.04536	131.79
0.8250	1.05547	131.94
1.0109	1.06698	132.06
1.1432	1.07484	132.14
1.2709	1.08215	132.26
1.4134	1.09013	132.31
1.6321	1.10183	132.41

KTS ^{O}C

m	d	$V_{2\Phi}$
0.0132	0.99327	131.43
0.1319	1.00245	131.80
0.6596	1.03964	132.58
0.8025	1.04896	132.54
0.9908	1.06058	132.72
1.1161	1.06799	132.84
1.4031	1.08422	133.00
1.6158	1.09578	132.96

RbTS 5 ^{O}C

m	d	$V_{2\Phi}$
0.0097	1.00120	129.67
0.0500	1.00626	129.86
0.0976	1.01216	130.11
0.2107	1.02586	130.40
0.3192	1.03854	130.76
0.4261	1.05073	130.89
0.5645	1.06587	131.26
0.6937	1.07957	131.44
0.8371	1.09415	131.74

RbTS 15 ^{O}C

m	d	$V_{2\Phi}$
0.0090	1.00021	133.79
0.0505	1.00526	134.05
0.4023	1.04562	134.79
0.7966	1.08633	135.38
1.0107	1.10672	135.61
1.0935	1.11433	135.67
1.2118	1.12500	135.71
1.3905	1.14036	135.91
1.5548	1.15397	136.02

RbTS 25 ^{O}C

m	d	$V_{2\Phi}$
0.0091	0.99814	136.09
0.0500	1.00303	136.30
0.1370	1.01320	136.55
0.3981	1.04220	137.12
0.7859	1.08163	137.49
1.0100	1.10259	137.71
1.0788	1.10878	137.80
1.2127	1.12056	137.88
1.3959	1.13617	137.92

RbTS 40 ^{O}C

m	d	$V_{2\Phi}$
0.0089	0.99329	136.59
0.0499	0.99816	136.88
0.1374	1.00835	137.19
0.3959	1.03701	137.55
0.7809	1.07606	137.95
0.9964	1.09632	138.06
1.0692	1.10296	138.06
1.1935	1.11387	138.20
1.3824	1.13000	138.24
1.5304	1.14200	138.37

CsTS 5 ^{O}C

m	d	$V_{2\Phi}$
0.0099	1.00160	137.62
0.0385	1.00633	137.84
0.0665	1.01091	137.99
0.3009	1.04777	138.60
0.4405	1.06854	138.89
0.5578	1.08530	139.23
0.6888	1.10344	139.44
0.8348	1.12290	139.66
1.2457	1.17346	140.44

CsTS 15 ^{O}C

m	d	$V_{2\Phi}$
0.0104	1.00078	141.37
0.0495	1.00709	141.54
0.1116	1.01694	141.77
0.7055	1.10246	142.83
0.8002	1.11487	142.88
0.9184	1.12981	143.06
1.0216	1.14251	143.19
1.1136	1.15360	143.23
1.2552	1.17014	143.32

CsTS 25 ^{O}C			CsTS 40 ^{O}C		
m	d	$V_{2\Phi}$	m	d	$V_{2\Phi}$
0.0494	1.00492	143.65	0.0103	0.99387	143.59
0.1099	1.01437	143.88	0.0490	1.00001	143.78
0.3445	1.04945	144.39	0.1099	1.00953	144.03
0.6945	1.09759	144.76	0.3434	1.04443	144.43
0.7977	1.11085	144.95	0.6904	1.09217	144.84
0.9103	1.12498	145.02	0.7931	1.10549	144.87
1.0184	1.13814	145.09	0.9039	1.11939	144.99
1.0955	1.14726	145.19	1.0118	1.13255	145.08
1.2307	1.16283	145.33	1.0874	1.14161	145.08
			1.2214	1.15713	145.21

The apparent molal volumes at infinite dilution $V_{2\Phi}^{o}$ were calculated using Equation (2) proposed by Redlich and Meyer [7]:

$$V_{2\Phi} - S_V c^{1/2} = V_{2\Phi}^{o} + b_V c \qquad (2)$$

where S_V (in dm$^{3/2}$-cm^{3}-mol$^{-3/2}$) is the Debye-Hückel limiting slope, which for 1:1 type electrolytes is the following function of temperature t (in ^{O}C) [12]

$$S_V = 1.4447 + 1.6799x10^{-2}\,t - 8.4055x10^{-6}\,t^2 + 5.5153x10^{-7}\,t^3 \qquad (3)$$

and b_V (in cm^{3}-dm^{3}-mol^{-2}) is the empirical deviation constant. The experimental results for LiTS and KTS are also shown graphically in Figures 1 and 2. The apparent molar volumes of alkaline p-toluenesulphonates at infinite dilution and the deviation constants b_V at various temperatures are collected in Table II. The possible experimental errors are given in parentheses.

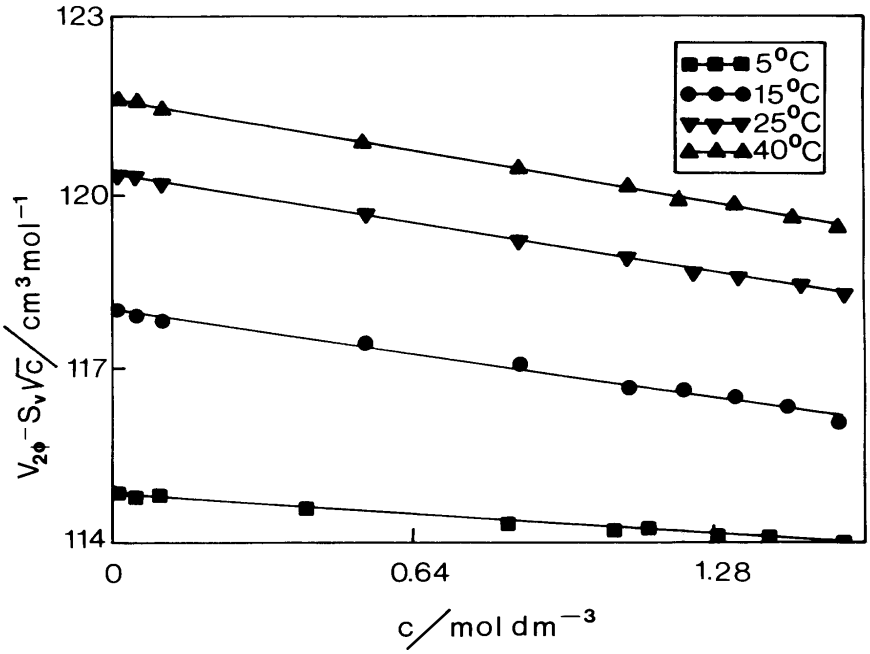

Figure 1. Plot of $V_{2\Phi} - S_V\sqrt{c}$ vs. molarity for LiTS in water at various temperatures; S_V from Equation (3).

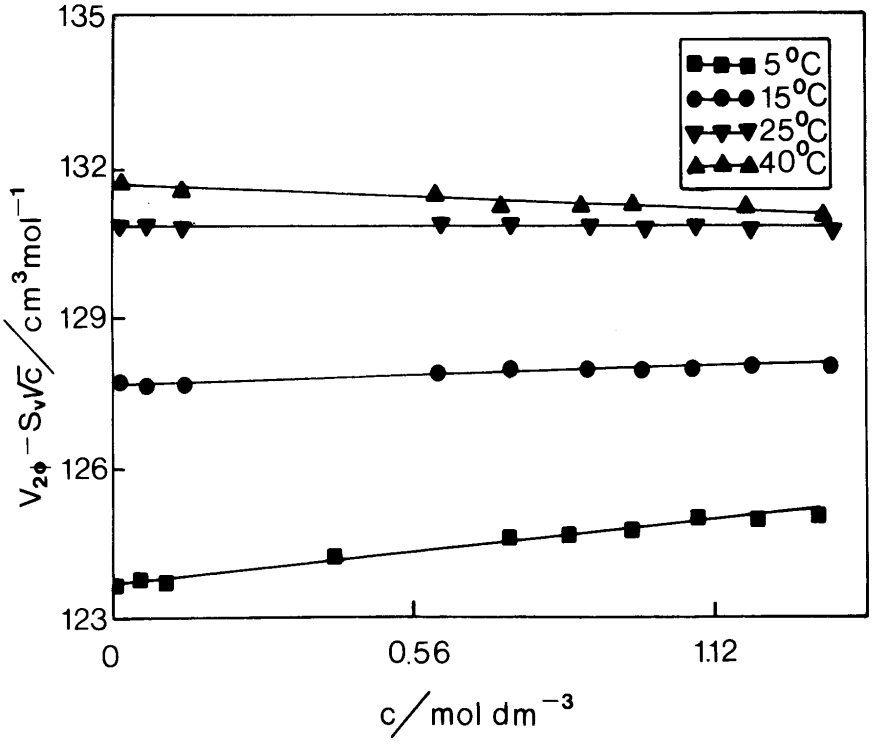

Figure 2. Plot of $V_{2\Phi}$ - $S_V \sqrt{c}$ vs. molarity for KTS in water at various temperatures; S_V from Equation (3).

TABLE II. Apparent Molar Volumes of Alkaline p-Toluenesulphonates at Infinite Dilution and the Deviation Constant b_V at Various Temperatures.

HTS			LiTS	
t[d]	$V_{2\Phi}^0$	b_V	$V_{2\Phi}^0$	b_V
5	115.36 (0.30)	-0.08 (0.30)	114.77 (0.24)	-0.48 (0.24)
15	118.27 (0.23)	-0.77 (0.23)	117.75 (0.25)	-1.08 (0.25)
25	120.57 (0.23)	-0.90 (0.23)	119.97 (0.24)	-1.24 (0.24)
40	121.95 (0.11)	-1.02 (0.11)	121.17 (0.25)	-1.31 (0.25)

[d] ^{0}C

NaTS			KTS	
t	$V_{2\Phi}^0$	b_V	$V_{2\Phi}^0$	b_V
5	114.63 (0.26)	0.87 (0.260)	123.68 (0.34)	1.04 (0.34)
15	117.47 (0.21)	0.19 (0.21)	127.38 (0.3)	0.29 (0.30)
25	119.67 (0.21)	-0.15 (0.21)	130.36 (0.30)	-0.05 (0.30)
40	120.49 (0.22)	-0.60 (0.22)	131.14 (0.44)	-0.44 (0.44)

RbTS			CsTS	
t	$V_{2\Phi}^0$	b_V	$V_{2\Phi}^0$	b_V
5	129.49 (0.96)	1.20 (0.96)	137.46 (0.64)	1.26 (0.64)
15	133.64 (0.55)	0.37 (0.55)	141.17 (0.62)	0.42 (0.62)
25	135.90 (0.47)	0.05 (0.47)	143.24 (0.60)	0.14 (0.60)
40	136.41 (0.42)	-0.38 (0.42)	143.35 (0.59)	-0.32 (0.59)

Discussion

The apparent molar volumes presented in this work cannot be compared directly with literature values since, to our knowledge, no such data were published. It is possible, however, to make some comparison of the temperature dependence of $V_{2\Phi}^0$ with those solutes for which data are available. To test the consistency of the experimental results, the additivity of the apparent molar volumes at infinite dilution at 25 ^{O}C was examined. The differences between the parameters $V_{2\Phi}^0$, Δ are given in Table III. One can notice that the differences Δ for alkaline p-toluenesulphonates are very close to those for alkaline chlorides. The discrepancies lie within the experimental error of the determination of $V_{2\Phi}^0$. This result is not unexpected since at the infinite dilution limit the ion-ion interactions vanish and the $V_{2\Phi}^0$ values represent only ion-water interactions.

In the case of complete dissociation the Δ values depend only on the difference by which different ions affect the structure of water.

Table III. Differences, Δ, of the $V_{2\Phi}^{0}$ Values for Alkaline Chlorides and Alkaline p-Toluenesulphonates at 25 ^{O}C.

Ion	Cl^- [10]	Δ	TS^-
Li^+	16.91	103.06	119.97
Δ	-0.29		-0.30
Na^+	16.62	103.05	119.67
Δ	10.19		10.69
K^+	26.81	103.55	130.36
Δ	5.13		5.54
Rb^+	31.94	103.96	135.90
Δ	7.23		7.34
Cs^+	39.17	104.07	143.24

To examine the effect of temperature on $V_{2\Phi}^{0}$ for alkaline p-toluenesulphonates, the results for $V_{2\Phi}^{0}$ were expressed as a polynomial function of temperature and the polynomial was then differentiated with respect to temperature. This way a function was obtained which allowed calculation of the apparent molar expansibility of the solute at the infinite dilution limit [12] :

$$E_{2\Phi}^{0} = \left(\partial V_{2\Phi}^{0} \Big/ \partial T \right)_{p} \qquad (4)$$

Figure 3 shows $E_{2\Phi}^{0}$ for Li and K p-toluenesulphonate solutions as a function of temperature. $E_{2\Phi}^{0}$ values for LiCl and KCl [12] are included in Figure 3 for comparison. The conclusion is that the values of $E_{2\Phi}^{0}$ for alkaline p-toluenesulfonate solutions decrease with increasing temperature, as in the case of other simple electrolytes.

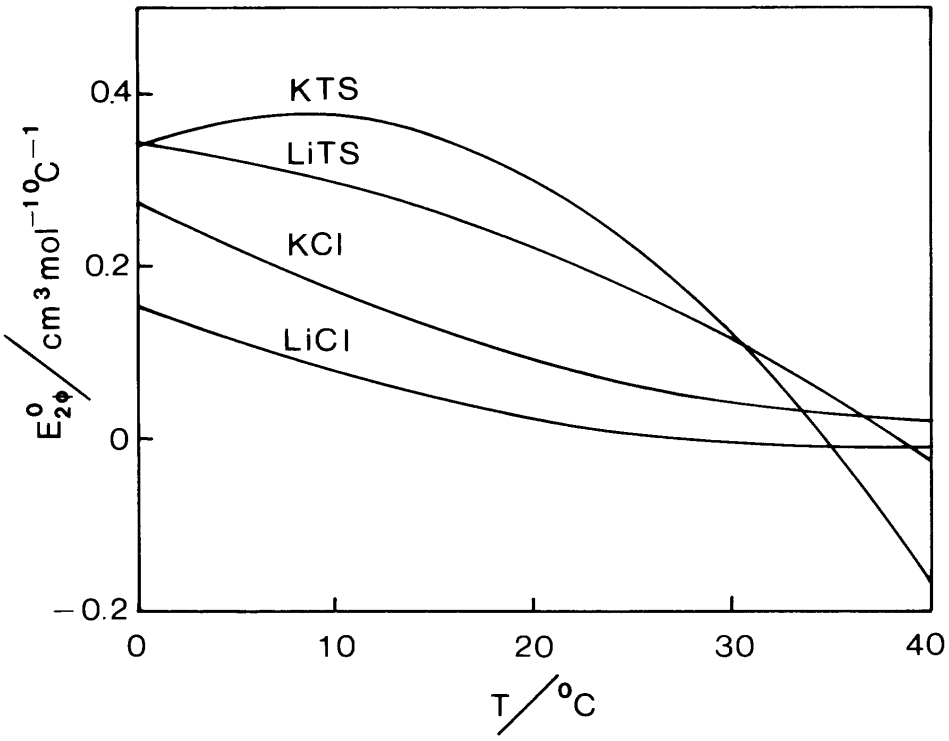

Figure 3. Partial molar expansibility of aqueous LiTS, KTS, LiCl and KCl at infinite dilution as a function of temperature.

There are, however, differences in the magnitude of $E_{2\Phi}{}^{0}$ and in the shape of the curve. It seems reasonable to attribute this effect to the influence of the large aromatic anion on the structure of water. (See also Figure 4). Hepler [14] has pointed out that from the thermodynamic relation

$$\left(\frac{\partial \bar{C}_P^{\,0}}{\partial P}\right)_T = -T\left(\frac{\partial^2 \bar{V}^{\,0}}{\partial T^2}\right)_P = -T\frac{\partial \bar{E}^{\,0}}{\partial T} \qquad (5),$$

where $\bar{C}_P{}^{0}$ is the partial molar heat capacity at infinite dilution, one can discern the type of effect. A positive value of $\left(\frac{\partial \bar{C}_P^{\,0}}{\partial P}\right)_T$, or a negative value of $\frac{\partial \bar{E}^{\,0}}{\partial T}$, is evidence of the structure breaking effect of the solute. It seems then reasonable to regard the ion of the aromatic electrolyte (cf. Figure 4) as having a dual character: it has a "structure making" effect on water on the aromatic side and a "structure breaking" effect on the side of the sulphonic group. The former effect expands, and the latter diminishes the apparent size

of an ion. Both types of effect are temperature dependent. At higher temperatures electrostriction becomes more important leading to a reduction of size [12].

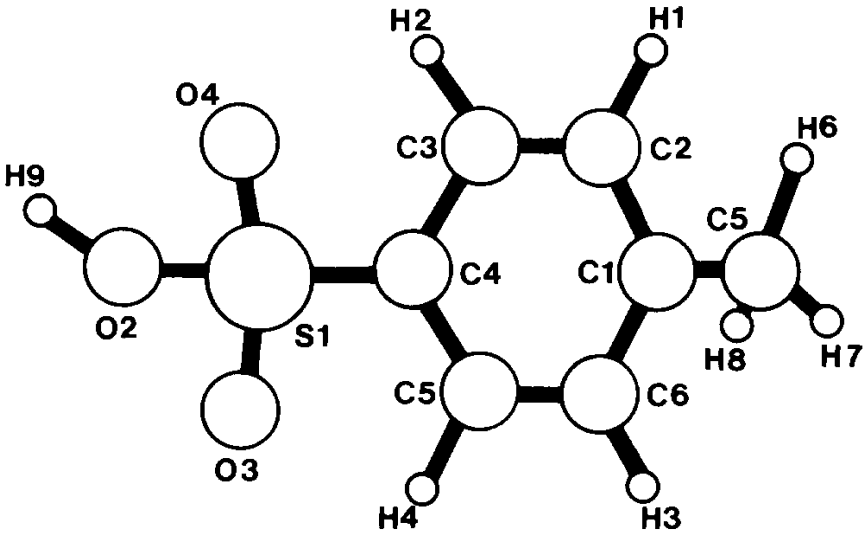

Figure 4. The structure of p-toluenesulphonic acid.

The values obtained for b_V in Equation (2) are tabulated in Table II. Since there is no theory that covers this empirical term it is not known what significance to attach to it, although it probably has to do primarily with solute-solute interactions. One can see, however, that b_V is positive at lower temperatures and becomes less positive or more negative, as the temperature rises. This behaviour is consistent with that found by Helgeson and Kirkham [15] for several inorganic salts, and recently also by Strong et al. [16] for some methyl substituted benzoic acids and their sodium salts.

Finally, it should be mentioned that direct comparison of the apparent molal volumes of polyelectrolytes with those of model electrolytes is not possible. Škerjanc [17] has demonstrated experimentally and theoretically a sharp fall of $V_{2\Phi}$ with decreasing polyelectrolyte concentration. These results lead to the conclusion that $V_{2\Phi}$ data obtained by linear extrapolation of $V_{2\Phi}$ to zero concentration [18,19] should be accepted with a great deal of caution. Furthermore, the apparent molar volumes of polyelectrolytes are not additive, the reason being the so-called site binding of counterions [20].

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Povzetek

Izmerili smo gostote raztopin alkalijskih soli p-toluensulfonske kisline pri temperaturah 5, 15, 25 in 40 ^{o}C in v koncentracijskem območju od 0.01 do 2 mol-kg^{-1}. Iz dobljenih podatkov smo izračunali navidezne molske volumne $V_{2\Phi}$. Z uporabo Redlich-Meyerjeve enačbe smo določili navidezne molske volumne pri neskončnem razredčenju $V_{2\Phi}^{o}$ in deviacijske parametre b_V. Ugotovili smo, da velja pravilo o aditivnosti navideznih ionskih volumnov pri temperaturi 25 ^{O}C. Vrednosti $V_{2\Phi}^{o}$ naraščajo, vrednosti parametrov b_V, pa padajo z naraščajočo temperaturo. Temperaturna odvisnost volumskih lastnosti raztopin alkalijskih p-toluensulfonatov je podobna temperaturni odvisnosti alkalijskih kloridov.